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# THE GIBBS QUANTUM ENSEMBLE AND ITS CONNECTION WITH THE CLASSICAL ENSEMBLE

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In this paper there is examined the limiting transition from the quantum equations of motion for the density matrix, describing the Gibbs ensemble in quantum mechanics, to the equation of motion for the classical distribution functions. The special condition of distinguishability of the particles is established.

The most general quantum ensemble of $N$ particles is described by the density matrix (by the statistical operator, according to von Neumann's nomenclature) $\rho$. The matrix elements of this matrix may be written in the following form:

$$(q_1 q_2 \ldots q_k \ldots q_N | \rho | q_1' q_2' \ldots q_k' \ldots q_N') = = (q | \rho | q'), \tag{1}$$

where the letter $q_k$ denotes the totality of the coordinates of the $k$th particle. The matrix $\rho$ satisfies the equation of motion:

$$ih \frac{\partial \rho}{\partial t} = H\rho - \rho H, \tag{2}$$

where $H$ is Hamiltonian for the system of particles being investigated. The following conditions are imposed upon the matrix $\rho$:

$$(q | \rho | q') = (q' | \rho | q)^* \tag{3}$$

(Hermitian conjugacy) and, if in addition the condition of indistinguishability of the particles is imposed, then

$$P_q (q | \rho | q') = \pm (q | \rho | q'), \tag{3a}$$
$$P_q' (q | \rho | q') = \pm (q | \rho | q'), \tag{3b}$$
$$P_q P_q' (q | \rho | q') = + (q | \rho | q'). \tag{3c}$$

Here $P_q$ denotes the permutation of the coordinates $q_i$ of the $i$th particle and the coordinates $q_k$ of the $k$th particle. In a similar manner $P_q'$ denotes the permutation of the $q_i'$ and the $q_k'$ coordinates. $P_q P_q'$ denotes the permutation of the $i$th and the $k$th particles. The plus or minus sign is taken according to whether the particles obey Bose or Fermi statistics, respectively. The condition of symmetry in the particles (3c) (indistinguishability of the particles) may be considered as a result of (3a) and (3b)*.

At a first glance both the matrix $\rho$ (1) and its equation (2) differ considerably from the classical distribution function $f(q, p)$ in the phase space ($p$ denotes the impulses of the particles) and from the equation which this distribution function satisfies, namely:

$$\frac{\partial f}{\partial t} = -\left(\frac{\partial H}{\partial p} \cdot \frac{\partial f}{\partial q} - \frac{\partial H}{\partial q} \cdot \frac{\partial f}{\partial p}\right) = -[H, f]_1, \tag{4}$$

where $H = H(p, q)$ denotes the classical Hamiltonian function for a system of particles **.

However, the connection between the classical distribution function $f(q, p)$ and the quantum matrix $\rho$ can be established if one turns to the so-called mixed representation $(p, q)$ of the matrix $\rho$. Therefore let us determine the matrix in the mixed repres-

* Conditions (3a) and (3b) are equivalent to the condition of symmetry or antisymmetry of wave functions with respect to the permutation of any pair of particles.

** We obviously choose here only one pair of canonical, conjugate coordinates and impulses $(p, q)$. We will proceed in the same manner in what follows also, since all our consideration are easily generalized for the case of any number of degres of freedom, except for one point which will be especially noted further on.

entation $(q|\rho|p)$ by means of Fourier transformation of the matrix $(q|\rho|q')$:

$$(q|\rho|p)=\int(q|\rho|q')\frac{e^{\frac{ipq'}{h}}}{\sqrt{2\pi h}}dq', \quad (5)$$

$$(q|\rho|q')=\int(q|\rho|p)\frac{e^{-\frac{ipq'}{h}}}{\sqrt{2\pi h}}dp. \quad (5')$$

In a similar manner, for any mechanical quantity $L$, let us introduce instead of the matrix elements $(q|L|q')$ the mixed elements:

$$(q|L|p)=\int(q|L|q')\frac{e^{\frac{ipq'}{h}}}{\sqrt{2\pi h}}dq', \quad (6)$$

$$(q|L|q')=\int(q|L|p)\frac{e^{-\frac{ipq'}{h}}}{\sqrt{2\pi h}}dp. \quad (6')$$

The mixed matrix elements may be replaced by new quantities which are connected with them by the following relations:

$$R(q,p)=(q|\rho|p)\,e^{-\frac{ipq}{h}}\sqrt{2\pi h}, \quad (7)$$

$$L(q,p)=(q|L|p)\,e^{-\frac{ipq}{h}}\sqrt{2\pi h}. \quad (8)$$

These new quantities, which are functions of $p$, $q$, fully replace the initial quantities $(q|\rho|q')$ and $(q|L|q')$.

Actually, assuming that $q'=q+\xi$ with the help of (5'), (6'), (7) and (8) we may obtain:

$$(q|\rho|q+\xi)=\int R(q,p)\frac{e^{-\frac{ip\xi}{h}}}{2\pi h}dp, \quad (7')$$

$$(q|L|q+\xi)=\int L(q,p)\frac{e^{-\frac{ip\xi}{h}}}{2\pi h}dp. \quad (8')$$

The quantity $L(q,p)$ (8) possesses the extraordinary properties that, if the corresponding classical quantity $L_{\text{class}}(q,p)$ does not contain the products of the noncommuting (in quantum mechanics) quantities, *i. e.* has the form $L_{\text{class}}(q,p)=f(q)+\varphi(p)$, then, the quantity $L(q,p)$, determined according to (8), is equal to $L_{\text{class}}(q,p)$. However, if such products are encountered (for example, $p\cdot q$), then $L(q,p)=L_{\text{class}}(q,p)+$ terms of a higher order with respect to $h$ *.

Therefore, it may be expected that not the matrix $(q|\rho|p)$ but the function $R(q,p)$, which we introduced, will be the analogue of the classical distribution function $f(q,p)$ and will tend to $f(q,p)$ when $h\to 0$.

This expectation is justified, although not in all respects (see below).

Before proceeding to the connection between $R(q,p)$ and $f(q,p)$, let us formulate conditions (3), (3a), (3b) and (3c), imposed on the matrix $\rho$, in terms of the new function $R$.

In order to deduce the condition of Hermitian conjugacy (3) with respect to $R(q,p)$ let us express $(p|\rho|q')=(q|\rho|q+\xi)$ in (3) in terms of $R(q,p)$ by means of (7'). Then we obtain without difficulty:

$$R^*(q,p)=\int R(q+\xi,p+\eta)\cdot e^{i\frac{\xi\eta}{h}}\cdot\frac{d\xi d\eta}{2\pi h}. \quad (9)$$

The condition of Hermitian conjugacy for $L(q,p)$ is formulated in exactly the same manner. In the case when $L(q,p)=f(q)+\varphi(p)$ it is altogether trivial, namely $L^*(q,p)=L(q,p)$.

The state of affairs with respect to the complementary condition of symmetry imposed upon the function $R(q,p)$ is altogether different. On the basis of (5), it follows (since the product $p\cdot q$ in the exponent is the sum $\sum_k p_k\cdot q_k$ in the case of several particles from (3a), (3b) and (3c) that

$$P_q(q|\rho|p)=\pm(q|\rho|p), \quad (3a')$$

$$P_p(q|\rho|p)=\pm(q|\rho|p), \quad (3b')$$

$$P_qP_p(q|\rho|p)=+(q|\rho|p). \quad (3c')$$

Furthermore, $P_q$ retains its former meaning, while $P_p$ denotes the permutation of the impulses $p_i$ and $p_k$ of the $i$th and $k$th particles.

On the basis of (7), from (3a'), (3b') and (3c') we obtain for $R(q,p)$:

$$P_qR(q,p)=\pm R(q,p)\,e^{-\frac{i}{h}(p_i-p_k)(x_i-x_k)}, \quad (10a)$$

$$P_pR(q,p)=\pm R(q,p)\,e^{-\frac{i}{h}(p_i-p_k)(x_i-x_k)}, \quad (10b)$$

$$P_qP_pR(q,p)=R(q,p). \quad (10c)$$

* See J. P. Terletzky's paper in the Journal of Experimental and Theoretical Physics (Журн. эксп. и теор. физ.) 1937. In this work attention is not paid to the connection between the considerations mentioned and both the general theory of transformation and the method of the density matrix

Thus we see that the latter condition (symmetry in the particles) does not contain $h$ and may be formulated in the classical manner. On the contrary, the special conditions of symmetry in the impulses and the coordinates (10a) and (10b) contains $h$, forming an essentially singular point.

The function $R(q, p)$, similar to $(q|\rho|q')$, permits one to calculate the average value of any quantity $L(p, q)$. Namely, if the quantity $L$ is represented by the operator $L$, then the average, value, $\overline{L}$, is:

$$\overline{L} = S_p(L\rho) = \int (q|L|q')(q'|\rho|q)\,dq\,dq'. \quad (11')$$

Here, expressing $(q|L|q')$ and $(q'|\rho|q)$ in terms of $L(q, p)$ and $R(q, p)$, respectively, with the aid of (7′) and (8′) we will get:

$$\overline{L} = \int \frac{d\xi\,d\eta\,dp\,dq}{(2\pi h)^2} e^{i\frac{\xi\eta}{h}} \cdot L(q, p) \times \\ \times R(q+\xi, p+\eta), \quad (11)$$

or

$$\overline{L} = \int \frac{dp\,dq}{2\pi h} L(q, p) \cdot R^*(q, p), \quad (12)$$

which is completely analogous to the classical average:

$$\overline{L} = \int \frac{dp\,dq}{2\pi h} L_{\text{class}}(q, p) \cdot f(q, p). \quad (11'')$$

Further it is easy to be convinced that the average value of (11) or (12) for the Hermitian operator $L$ is real as it should be *.

Substituting $R(q, p)$ for $(q|\rho|q')$ in equation (2) [with the aid of (7)], and $H(q, p)$ for $(q|H|q')$ [with the aid of (8)], we obtain the equation of motion for $R(q, p)$:

$$ih\,\frac{\partial R(q, p)}{\partial t} = \\ = \int \frac{d\xi\,d\eta}{2\pi h} e^{-i\frac{\xi\eta}{h}} \{H(q, p+\eta)\,R(q+\xi, p) - \\ - H(q+\xi, p)\,R(q, p+\eta)\} \quad (12)$$

where $H(q, p)$ is nothing more than the classical Hamilton function of a system of particles. It is not difficult to verify that conditions (9) and (10) are invariant, i. e. holding for any moment, they still continue to hold for all moments also.

* For this (9) must be employed, applying it to $L(q, p)$.

For the purpose of establishing the connection with the equation for the classical distribution function (4), let us expand $R$ and $H$ in (9) and (12) into powers of $\xi$, $\eta$. Then we obtain a sum of the integrals of the form:

$$I_{nm} = \int\limits_{-\infty}^{+\infty}\int \frac{d\xi\,d\eta}{2\pi h} e^{\pm i\frac{\xi\eta}{h}} \cdot \xi^n \cdot \eta^m. \quad (13)$$

These integrals may be easily calculated with the aid of $\delta$-function. Actually,

$$I_{nm} = \left(\pm\frac{h}{i}\right)^m \int\limits_{-\infty}^{+\infty}\int \frac{\xi^n d\xi\,d\eta}{2\pi h} \cdot \frac{\partial}{\partial\xi^m} e^{\pm i\frac{\xi\eta}{h}} = \\ = (\mp ih)^m \cdot \int\limits_{-\infty}^{+\infty} \xi^n \cdot \frac{d^m\delta(\xi)}{d\xi^m} \cdot d\xi = \\ = (\pm ih)^m \cdot m!\,\delta_{nm}, \quad (13')$$

where $\delta_{nm} = 1$, when $n = m$, and $\delta_{nm} = 0$, when $n \neq m$.

Making use of this formula, instead of (9) and (12) we get:

$$R^*(q, p) = \sum_{n=0}^{\infty} \frac{(ih)^n}{n!} \frac{\partial^{2n} R(q, p)}{\partial p^n\,\partial q^n}, \quad (14)$$

$$\frac{\partial R(q, p)}{\partial t} = -\sum_{n=1}^{\infty} \frac{(-ih)^{n-1}}{n!} [H, R]_n, \quad (15)$$

where

$$[H, R]_n = \frac{\partial^n H}{\partial p^n} \cdot \frac{\partial^n R}{\partial q^n} - \frac{\partial^n H}{\partial q^n} \cdot \frac{\partial^n R}{\partial p^n} \quad (16)$$

is the Poisson bracket of the $n$th order*.

In order that these equations might give an approximation to the classical equation with $h \to 0$, it is necessary to be able to expand $R$ into powers of $h$. This can only be accomplished if we neglect the conditions for symmetry or antisymmetry (10a) and (10b).

In particular, these conditions are absent in general for the Gibbs ensemble, formed by systems consisting of one particle or of dissimilar (indistinguishable) particles.

Then, taking the expansion:

$$R = \sum_{n=0}^{\infty} R_n h^n \quad (17)$$

* Equations (15) and (16) are easily generalized for any number of degrees of freedom.

instead of (14) and (15) we obtain a system of equations for the function $R_n$*:

$$R_n^* = \sum_{h=0}^{k \leqslant n} \frac{i^k}{k!} \frac{\partial^{2k} R_{n-k}}{\partial p^k \partial q^k}, \qquad (14')$$

$$\frac{\partial R_n}{\partial t} = - \sum_{h=0}^{k \leqslant n+1} \frac{(-i)^{k-1}}{k!} \cdot [H, R_{n+1-k}]_k; \qquad (15')$$

the first equation of each system of equations running as follows:

$$R_0 = R_0^*, \quad R_1^* = R_1 + \frac{i}{1!} \frac{\partial^2 R_0}{\partial q\, \partial q},$$

$$R_2^* = R_2 + \frac{i}{1!} \frac{\partial^2 R_1}{\partial p\, \partial q} - \frac{1}{2!} \frac{\partial^4 R_0}{\partial p^2 \partial q^2}, \ldots \qquad (14'')$$

$$\frac{\partial R_0}{\partial t} = -[H, R_0]_1, \quad \frac{\partial R_1}{\partial t} = -[H, R_1]_1 + + \frac{i}{2!}[H, R_0]_2, \quad \frac{\partial R_2}{\partial t} = -[H, R_2]_1 + + \frac{1}{2!}[H, R_1]_2 + \frac{1}{3!}[H, R_0]_3, \ldots \qquad (15'')$$

In particular, the equation for $R_0$ agrees exactly with equation (4) for the classical distribution function $f(q, p)$ and this proves the direct connection between $R(q, q)$ and $f(q, p)$.

At the same time we must come to the conclusion that the condition of the indistinguishability of the particles is «more quantum» than the equations of motion, since while fulfilling this condition $R$ cannot be expanded into powers of $h$.

The reason for this latter circumstance, expressed by condition (10), may be discerned most easily if we turn to the representation of the matrix $\rho$ given in (1) [similar considerations may be given in the $(q, p)$ representation also].

The wave functions $\psi(q)$ [and also $\psi(p)$], as is known, cannot be expanded with respect to the $h$ powers, and when $h \to 0$, they tend to

$$\psi(q) = A(q)\, e^{i \frac{S(q)}{h}}$$

where $S(q)$ is the action function. On the other hand, the matrix $\rho$ is a bilinear formation in $\psi(q)$, the typical term of which will be:

$$\psi(q)\, \psi^*(q') = A(q)\, A(q')\, e^{\frac{i}{h}[S(q) - S(q')]}$$

and for the diagonal terms $(q = q')$ it does not contain $h$ in the exponent. Therefore, the bilinear formation $\rho$ may be expanded into powers of $h$. This holds for an ensemble composed of many particles also, since the condition of symmetry and anitsymmetry of $\psi$ is not imposed. However, if this condition is kept, the state of affairs will be different, which is easy to explain by using two particles as an example. In this case the symmetrized functions $\psi(q_1 q_2)$ will be

$$\psi(q_1 q_2) = A(q_1 q_2)\, e^{\frac{i}{h} S(q_1 q_2)} \pm \pm A(q_2 q_1)\, e^{\frac{i}{h} S(q_2 q_1)}$$

here the plus sign is taken for Bose statistics, while the minus sign for Fermi statistics. The typical term in $(q \mid \rho \mid q')$ in this case will be:

$$\psi(q_1 q_2)\, \psi^*(q_1' q_2') = A(q_1 q_2)\, A(q_1' q_2')\, e^{\frac{i}{h}[S(q_1 q_2) - S(q_1' q_2')]} + A(q_2 q_1)\, A(q_2' q_1') e^{\frac{i}{h}[S(q_2 q_1) - S(q_2' q_1')]} \pm$$
$$\pm A(q_2 q_1)\, A(q_1' q_2')\, e^{\frac{i}{h}[S(q_2 q_1) - S(q_1' q_2')]} \pm A(q_1 q_2)\, A(q_2' q_1')\, e^{\frac{i}{h}[S(q_1 q_2) - S(q_2' q_1')]},$$

therefore, the diagonal term will be:

$$\psi(q_1 q_2)\, \psi^*(q_1 q_2) = A(q_1 q_2)\, A(q_1 q_2) + A(q_2 q_1)\, A(q_2 q_1) \pm$$
$$\pm 2A(q_1 q_2)\, A(q_2 q_1) \cos\left\{\frac{1}{h}[S(q_1 q_2) - S(q_2 q_1)]\right\}$$

*i. e.* it contains the Plank constant $h$ in a singular manner.

Thus, the quantum function $R(q, p)$ is approximated (with $h \to 0$) by the classical function $f(q, p)$ only for an ensemble of different (differing slightly in any way, but nevertheless not similar) particles.

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* We may become convinced without great difficulty that, as soon as equation (15′) is fulfilled for $R_n$, then the equation for $R_n^*$ is fulfilled identically in virtue of (14′), *i. e.* the condition (14′) is invariant.